On the other hand, if it is over 30% of the total thickness of the laminate tubular film, the impact strength of the laminate tubular film at low temperatures is reduced.

As the polyolefin of the outer layers, high density polyethylene, middle density polyethylene, low density poly-ethylene, ionomers, a copolymer of ethylene and vinyl acetate, a copolymer of ethylene and an ester of acrylic acid, a copolymer of ethylene and propylene, polypropylene, a copolymer of ethylene and α-olefin (the so-called linear low density polyethylene, hereinafter referred to as LLDPE), a polybutene and mixture thereof may be mentioned.

The preferable embodiments of the outer layers from the viewpoint of stretchability of the layer(s) are as follows.

i) At least one of outer layers is EVA of a crystal melting point of from 80 to 103°C.

ii) One of the outer layers is EVA of a crystal melting point of 80 to 103°C, and the other of the outer layers is LLDPE of a crystal melting point of from 110 to 130°C.

iii) One of the outer layers is EVA of a crystal melting point of 80 to 103°C, and the other of the outer layers is a mixture of not more than 40% by weight of the LLDPE of a crystal melting point of 110 to 130°C and not less than 60% by weight of the EVA of a crystal melting point of 80 to 103°C.

iv) Both the outer layers are the mixture of not more than 40% by weight of LLDPE of a crystal melting point of 110 to 130°C and not less than 60% by weight of the EVA of a crystal melting point of 80 to 103°C.

Of the four embodiments, i), ii) and iii) are preferable, particularly i) is more preferable, from the viewpoint of transparency of the thus prepared layer(s).

In addition, the total thickness of the layer(s) of the polyolefin is preferably in a range of from 40 to 92% of the total thickness of the heat-shrinkable laminate tubular film according to the present invention.

The use of at least one polyamide or thermoplastic polyester layer as the intermediate layer(s) is the characteristic feature of the heat-shrinkable laminate film according to the present invention, and by having the layer(s) of polyamide or thermoplastic polyester of an adequate rigidity and a favorable stretchability as intermediate layer, the stretchability and the rigidity of the laminate film comprising a VDC layer and the polyolefin layer(s) have been improved.

The laminate film disposed with two polyamide or thermoplastic polyester layers as intermediate layers between two outer layers of polyolefin and a core layer of VDC with adhesive layers is preferable.

As the polyamide, a polymer having a crystal melting point of not more than 240°C, preferably of 220°C is used and for instance, Nylon 6-66 (copolymer consisting of Nylon 6 and Nylon 66), Nylon 610 (polyhexamethylene sebacamide), Nylon 612 (a condensate of hexamethylenediamine and 1,10-decanedicarboxylic acid), Nylon 11(a condensate of 11-aminoundecanoic acid), Nylon 12 (a ring-open polymerizate of laurolactum) and Nylon 6 (polycapramide) may be exemplified.

0149321

As the thermoplastic polyester, a polymer having a crystal melting point of not more than 240°C, preferably not more than 220°C or showing no crystal melting point is used and the thermoplastic polyester comprises the acid moiety selected from an aromatic dibasic acid and an aliphatic dibasic acid and the glycol moiety selected from aliphatic glycol, cycloaliphatic glycol and aromatic glycol. As such an esters, for instance, Vylon (made by TOYOBO Co., Ltd.), Hytel (made by Goodyear Co., Ltd.) and PET-G (made by Eastman Kodak Co., Ltd.) may be exemplified.

For reference, the "crystal melting point" used in the present invention is the maximum temperature on a melting curve obtained by the determination on a specimen in an amount of 8 mg while using a differential scanning calorimeter (made by Perkin-Elmer Co., Model IB) at a rate of raising the temperature of 8°C/min.

In the case where the crystal melting point of the polyamide or the thermoplastic polyester is over 240°C, it is necessary to raise the extruding temperature, thereby the coextrusion of the polyamide or the thermoplastic polyester with VDC becomes difficult.

In the case where the heat-shrinkable laminate tubular film according to the present invention contains not less than two intermediate layers of the polyamide or the thermoplastic polyester, the two layers may be the same as each other or different from each other. It is necessary that the thickness of such layer is from 5 to 40%, more preferably

from 5 to 20% of the total thickness of the laminate tubular film according to the present invention. When the number of such layers is not less than 2, the total thickness of such layers is from 5 to 40% of the total thickness of the laminate tubular film according to the present invention. On the other hand, where the thickness of such layer(s) is below 5% of the total thickness of the laminate tubular film according to the present invention, such layer(s) cannot contribute to the rigidity of the laminate tubular film, and in the case of over 40%, coextrusion with the VDC is difficult. From the viewpoint of co-extrudability with the VDC, the thickness of such layer(s) is more preferably not more than 20% of the total thickness of the laminate tubular film according to the present invention.

As the adhesive material forming the adhesive layer, EVA containing from 13 to 28% by weight of vinyl acetate units, a copolymer of ethylene and an ester of acrylic acid containing from 13 to 28% by weight of the ester of acrylic acid, a modified copolymer of ethylene and an ester of acrylic acid with an unsaturated carboxylic acid and a material obtained by further modifying the thus modified copolymer with a metal may be exemplified. Of the above adhesives, modified copolymer of ethylene and an ester of acrylic acid with the unsaturated carboxylic acid, and the material obtained by further modifying the thus modified copolymer of ethylene and an acrylic ester, with a metal are more preferable.

0149321

Any one of the above-mentioned adhesive layer is disposed between the polyolefin layer and the VDC layer, between the VDC layer and the polyamide or the thermoplastic polyester layer, and between the polyolefin and the polyamide or thermoplastic polyester layer.

The thickness of an adhesive layer is preferably from 0.5 to 3 µm, and the total thickness of the adhesive layers is preferably from 20 to 120 µm.

In the preparation of the heat-shrinkable laminate tubular film, a plurality of resins each of which constructs a layer of the object laminate tubular film are respectively co-extruded from a common annular die connected to a plurality of extruders corresponding to a plurality of resins, thereby being extruded from the die as a laminate tubular film.

An assembling part of an example of such an annular die is schematically shown in Fig. 1 in which 7 is a passage of the assembled flow of the molten resins and the respective passages of the molten polyolefin, the molten VDC, the molten polyamide or the molten thermoplastic polyester, the molten polyolefin and the molten adhesive agent are shown by 1, 2, 4, 6 and 8. As shown in Fig. 1, it is preferable to provide the respective adiabatic spaces 3 and 5 on both sides of the passage for molten polyamide or molten thermoplastic polyester. By the thus provided adiabatic spaces, even in the case where the thermoplastic polyester is extruded at a high temperature, since the direct heat transfer to the VDC layer therefrom can be prevented, the VDC which is relatively apt

to be decomposed can be coextruded with the thermoplastic polyester or the polyamide. In the case of preparing a laminate flat film by using a T-die, the both end parts of the layer of the VDC coextruded with the polyamide layer or the thermoplastic polyester layer are apt to be decomposed and accordingly, such an operation is not favorable.

Although the order of lamination of the layers is optional as far as both of the outer layers are a polyolefin, the arrangement of the layers in the laminate tubular film is preferably in the following order from the outer layer to the inner layer:

polyolefin layer/adhesive agent layer/VDC layer/ adhesive resin layer/polyamide layer or the thermoplastic resin layer/adhesive resin layer/polyolefin layer.

The thus extruded laminate tubular film is stretched biaxially following the conventional biaxial inflation method to form the heat-shrinkable laminate tubular film according to the present invention.

Since the thus prepared, heat-shrinkable laminate tubular film of the present invention shows gas-barrier property and an adequate rigidity, it is suitably used in packaging particularly foodstuffs.

The present invention will be explained more in detail while referring to the following non-limitative examples.

EXAMPLES 1 TO 5 AND COMPARATIVE EXAMPLES 1 TO 3:

The VDC, the adhesive agent, the polyamide, the

thermoplastic polyester and the polyolefin respectively shown in Table 1 were extruded from a plurality of extruders, respectively, and the thus extruded, molten resins were supplied, particularly in Examples 1 to 5, to the annular co-extruding die provided with the adiabatic spaces (3 and 5) shown in Fig. 1, thereby extruding the thus supplied molten resins as a laminate tubular film. The thus prepared laminate tubular film was cooled in a quenching bath at 15 to 25°C to form a laminate tubular film of 120mm in folded width and 540μm in thickness. A small amount of soy-bean oil had been introduced into the inside space of the tubular film for the prevention of self-adherence of the inner layer when folded.

Then, the laminate tubular film was transferred through a hot water bath at a temperature shown in Table 3 at a transferring speed of 20 m/min and heated for about 12 sec while being pinched by the first pair of nip-rolls rotating at a speed of 20 m/min. Thereafter, the thus heated tubular film was taken out from the hot water bath and was stretched between the first pair of nip-folls rotating at a speed of 20 m/min and the second pair of nip-rolls rotating at a speed of 60 m/min, into the longitudinal direction at a stretched ratio of 3 (i.e. 60/20=3) while simultaneously being stretched to the diametrical direction 3 times by air supplied into the inside space of the tubular film. The thus obtained, biaxially stretched laminate film was 350mm in folded width and about 60 micrometer in thickness.

Table 1

Properties of Resins used

Resin	Density	Melt index (g/10min)	Crystal melting point (°C)	Remarks
VDC[1)]	-	-	-	
Polyamide	1.14	-	215	Nylon 6-66 made by TORAY Co., Ltd.
Thermoplastic polyester	1.267	-	not shown	PET-G, made by Eastman Kodak Co., Ltd.
LLDPE	0.922	2.5	122	Made by MITSUITOATSU Co., Ltd.
EVA-1	0.933	1.1	96	Content of vinyl acetate units of 5.5% by weight
EVA-2	0.93	1.5	91	Content of vinyl acetate units of 10% by weight
EVA-3	0.94	0.6	82	Content of vinyl acetate units of 15% by weight
N-polymer (as adhesive)[2)]	0.95	6	-	

Notes

1): A resinuous mixture of 100 parts by weight of a copolymer of vinylidene chloride (70% by weight) and vinyl chloride (30% by weight) and 1 part by weight of an epoxidized soy-bean oil.

2): A modified copolymer of ethylene and an ester of acrylic acid, obtained by modifying the copolymer of ethylene and an ester of acrylic acid with an unsaturated carboxylic acid, made by Nippon Petrochemical Co., Ltd.

0149321

-15-

Table 2

Item	Method
Shrinkage in hot water	After immersing a specimen (10 cm square) of each of the laminate films at a relaxed state thereof in hot water at 90°C for one min, the percentage of the length to the original length and the percentage of the width to the original width are shown, respectively as the averaged values of the test data on 20 specimens.
Gas-barrier property	The volume of gaseous oxygen (ml/m^2 of the film·24 hours·atm) permeated through a specimen of each of the laminate films at 30°C and relative humidity of 100%, respectively as the averaged values of the test data on 3 specimen.

Table 3

Layer Construction of Tubular Film and Temperature of Hot Water Bath

Examples and Comparative Example	Layer Construction							Temperature of Hot Water Bath (°C)
	1st layer (μm)	2nd layer (μm)	3rd layer (μm)	4th layer (μm)	5th layer (μm)	6th layer (μm)	7th layer (μm)	
Ex. 1	EVA-3 (12)	N-polymer (1)	VDC (8)	N-polymer (1)	Polyamide (6)	N-polymer (1)	EVA-3 (31)	85
Ex. 2	EVA-3 (12)	N-polymer (1)	VDC (8)	N-polymer (1)	PET-G (6)	N-polymer (1)	EVA-3 (31)	87
Ex. 3	LLDPE/EVA-1*1 (12)	N-polymer (1)	VDC (10)	N-polymer (1)	Polyamide (6)	N-polymer (1)	LLDPE/EVA-2*2 (29)	94
Ex. 4	LLDPE (9)	N-polymer (1)	VDC (8)	N-polymer (1)	PET-G (6)	N-polymer (1)	EVA-2 (34)	95
Ex. 5	LLDPE/EVA-1*1 (12)	N-polymer (1)	VDC (10)	N-polymer (1)	Polyamide (4)	N-polymer (1)	EVA-1 (31)	93
Comparat. Ex. 1	EVA-3 (15)	N-polymer (1)	VDC (8)	N-polymer (1)	EVA-3 (6)	N-polymer (1)	EVA-3 (28)	89
Comparat. Ex. 2	EVA-3 (12)	N-polymer (1)	VDC (4)	N-polymer (1)	Polyamide (15)	N-polymer (1)	EVA-3 (26)	-
Comparat. Ex. 3	LLDPE/EVA-1*1 (7)	N-polymer (1)	VDC (8)	N-polymer (1)	PET-G (27)	N-polymer (1)	LLDPE/EVA-2*2 (15)	98

Notes: *1: A mixture of 30 parts by weight of LLDPE and 70 parts by weight of EVA-1

*2: A mixture of 30 parts by weight of LLDPE and 70 parts by weight of EVA-2.

Table 3-2: Physical Properties of Tubular Film

Example or Comparative Example	Stretch-ability	Rigidity	Rate of heat-shrinkage (longitudinal/transversal)	Gas-barrier property	Coextrudability of tubular film
Example 1	A	A	51 / 53	58	A
Example 2	A	A	55 / 56	59	A
Example 3	A	A	43 / 45	50	A
Example 4	A	A	44 / 46	59	A
Example 5	A	A	45 / 47	50	A
Comparative Example 1	B	C	50 / 53	60	A
Comparative Example 2	-	-	-	-	C
Comparative Example 3	C	-	-	-	B

(Notes)

1) Stretchability:

A: Excellent, particularly excellently stretchable with unevenness of the thickness of the film of below 30%,

B: Inferior, although stretchable, with unevenness of the thickness of the film of from 30 to 50%,

C: Poor, although stretchable, without steadiness and with unevenness of the thickness of the film over 50%.

2) Rigidity:

A: Excellent, defects in the packaging operation such as the elongation of the film due to the content scarcely occur,

B: Inferior, defects in the packaging operation occur some times,

C: Poor, defects in the packagkng operation are apt to occur.

3) Coextrudability of the layers into a composite laminate tube:

A: Coextrusion was possible continuously for more than 10 hours,

B: The time of sufficient, continuous extrusion was below 10 hours,

C: Coextrusion could be continued only less than one hour.

As are clearly seen in the results of Examples 1 to 5 shown in Table 3, the heat-shrinkable laminate tubular film according to the present invention is excellent in stretchability and adequate rigidity, thereby excellent in processability in the packaging operation. In addition, the

combination of the resins for producing the film was excellent in cnextrudability.

On the other hand, although the resin combination of Comparative Example 1 was excellent for coextruding, the rigidity of the film was poor resulting in the poor processability in the packaging operation due to the absence of the layer of the polyamide or the thermoplastic polyester.

Although the resin combination of Comparative Example 2 includes the polyamide for the inner layer, because of the too thin layer of the VDC, decomposition of the VDC occurred to inhibit the continuous operation of coextrusion. In Comparative Example 3, because of the too large thickness of the layer of the thermoplastic polyester, the coextrudability was poor to cause the decomposition of the VDC. In addition, the coextruded film was poor in stretchability. By the above-mentioned demerits, any favorable laminate film could not be obtained.

0149321

CLAIMS:

1. A heat-shrinkable laminate tubular film comprising a gas-barrier layer of a copolymer of vinylidene chloride having a thickness of not less than 6μm and not more than 30% of the total thickness of the tubular film, outer layers of a polyolefin, at least one intermediate layer of a polyamide or a thermoplastic polyester having a crystal melting point of not more than 240°C and a thickness of 5 to 40% of the total thickness of the tubular film, and adhesive layers disposed between any of the above layers.

2. A heat-shrinkable laminate tubular film according to claim 1, wherein at least one of the outer layers is a copolymer of ethylene and vinyl acetate of a crystal melting point in a range of from 80 to 103°C.

3. A heat-shrinkable laminate tubular film according to claim 2, wherein one of the outer layers is a linear low-density polyethylene of a crystal melting point in a range of from 110 to 130°C or a mixture of not more than 40% by weight of the linear low-density polyethylene and not less than 60% by weight of a copolymer of ethylene and vinyl acetate of a crystal melting point in a range of from 80 to 103°C.

4. A heat-shrinkable laminate tubular film according to claim 1, wherein each of the outer layers is a mixture of not more than 40% by weight of a linear low-density polyethylene of a crystal melting point in a range of from 110 to 130°C and not less than 60% by weight of a copolymer of ethylene and vinyl

acetate of a crystal melting point in a range of from 80 to 103°C.

5. A heat-shrinkable laminate tubular film according to claim 1, wherein the total thickness of the heat-shrinkable laminate tubular film is in a range of from 20 to 120 micrometers,

the thickness of the gas-barrier layer is more than 6µm and not more than 25% of the total thickness of the heat-shrinkable laminate tubular film,

the thickness of the outer layer is in the range of 40 to 92% of the total thickness of the heat-shrinkable laminate tubular film,

the thickness of the intermediate layer(s) of a polyamide or a thermoplastic polyester is in the range of 5 to 20% of the total thickness of the heat-shrinkable laminate tubular film, and

the thickness of each of adhesive layers is 0.5 to 3.0µm.

6. Process for producing a heat-shrinkable laminate tubular film according to claim 1, comprising

feeding a copolymer of vinylidene chloride as a gas-barrier layer, a polyolefin as outer layers, a polyamide or a thermoplastic polyester as at least one intermediate layer and an adhesive material as adhesive layers to an annular die provided with passages for the gas-barrier layer, the outer layers, the intermediate layer(s) and the adhesive layers and

with adiabatic spaces disposed on the both sides of the passage(s) of the intermediate layer(s), in a molten state, the end portions of the passages of the gas-barrier layer, the outer layers, the intermediate layer(s) and the adhesive layers emerging into a common outlet of the annular die.

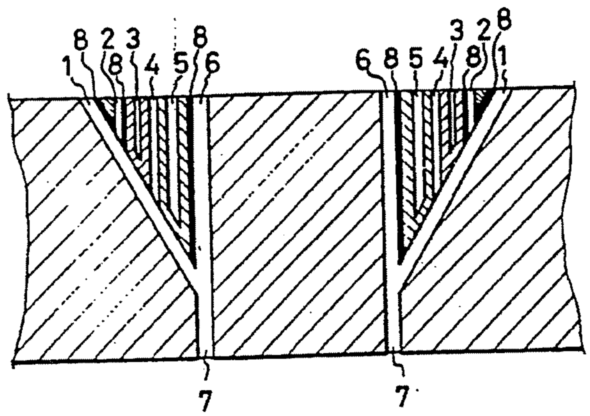
laminating and extruding the copolymer of vinylidene chloride, the polyolefin, the polyamide or the thermoplastic polyester and the adhesive material, thereby forming laminate tubular film at the outlet of the annular die,

cooling the resultant laminate tubular film by quenching, and

after heating the laminate tubular film, biaxially stretching the resultant laminate tubular film, thereby forming a heat-shrinkable laminate tubular film.

0149321

Fig. 1



European Patent Office

EUROPEAN SEARCH REPORT

0149321
Application number

EP 84 30 8302

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
X	GB-A-1 591 424 (GRACE) * Page 2, lines 115-129; page 3, lines 24-33; page 4, lines 40-63, 79-120 *	1	B 65 D 75/00 B 32 B 27/08 B 65 D 65/40
A		2	
A	* Page 4, lines 46-85 *	5	

X	FR-A-2 211 339 (DOW CHEMICAL) * Claim 12; figures 1-3 *	6	

A	GB-A-1 422 358 (DOW CHEMICAL) * Page 3, example 1 *	1	
	-----		TECHNICAL FIELDS SEARCHED (Int. Cl 4)
			B 32 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-03-1985	VAN THIELEN J.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO Form 1503 03 82

MAIL ROOM
FEB 17 1997

(12) UK Patent Application (19) GB (11) 2 139 948 A

6117

SUBJ.

41196

(43) Application published 21 Nov 1984

(21) Application No 8313717

(22) Date of filing 18 May 1983

(71) Applicant
British Cellophane Limited (United Kingdom),
Bath Road, Bridgwater, Somerset TA6 4PA

(72) Inventors
Derek James Dobbie,
Paul Kenyon Williamson

(74) Agent and/or Address for Service
Boult Wade & Tennant,
27 Furnival Street, London EC4A 1PQ

(51) INT CL³
B32B 27/08 27/30 27/32

(52) Domestic classification
B5N 2708 2730 2732
U1S 1814 3025 3028 B5N

(56) Documents cited
GB 1238215

(58) Field of search
B5N

(54) **Multilayer packaging film**

(57) A multilayer packing film having improved properties of oxygen permability, transparency, flexibility and toughness and capable of being converted into pouches and bags upon conventional packaging machinery without distortion under heat-sealing conditions comprises a surface layer of a heat-sealable polymer, preferably a linear low density polyethylene, an oxygen barrier layer, of an ethylene/vinyl alcohol copolymer and a layer of polypropylene having an atactic content of 10% to 25% by weight which has a melting point substantially greater than the heat-sealable polymer, optionally bonded by a polymeric adhesive and preferably manufactured by coextrusion.

The multilayer film is particularly useful for packaging liquids where a high degree of resistance to cracking is required.

GB 2 139 948 A

SPECIFICATION

Multilayer packaging films

This invention is concerned with multilayer packaging films and in particular to films of high oxygen impermeability, transparency, flexibility and toughness.

Films of high oxygen impermeability are particularly useful for packaging foodstuffs, including liquids, which are spoilt by prolonged contact with oxygen. They normally comprise two or more layers including an outer layer of a readily heat-sealable polymer such as low density polyethylene together with an oxygen barrier layer such as an ethylene vinyl alcohol copolymer layer, a vinylidene chloride copolymer layer or a polymer layer carrying a metallised coating such as an aluminium coating formed by vacuum deposition.

Films, especially for use in packaging liquids, are preferably transparent sufficiently for the contents of the packages to be viewed and are required to be tough and flexible to withstand rough handling during transport so as to avoid cracking and pin-holing which would lead to leaking of contents from the packages and break down of the oxygen barrier.

One cause of physical weakness in films of the prior art arises from heat-sealing operations when the films are made into bags or pouches on conventional heat-sealing machinery. During such operations, films are brought together, heat-sealable surface to heat-sealable surface, and are sealed together by pressure between heated reciprocating heat-sealing jaws. All the layers of the film are softened, the film temporarily becomes more stretchable in the heat-seal area and under the influence of the tension in the film drawing the film through the machine there is a distinct tendency for the film to stretch and distort in the heat-seal area.

The object of the present invention is to provide improved multilayer packaging films having high oxygen impermeability and toughness.

According to the present invention a multilayer heat-sealable film having a high oxygen impermeability comprises a surface layer of a heat-sealable polymer capable of forming seals of adequate strength with itself under pressure at a temperature from about 80°C to about 130°C, an oxygen barrier layer of an ethylene vinyl alcohol copolymer and a layer of polypropylene having an atactic content in the range from about 10% to about 25% by weight.

Adjacent layers may conveniently be bonded together by a suitable "tie layer" consisting of a polymeric adhesive such as a polyolefin grafted with a monomer having polar functional groups. A suitable adhesive for use in this application is a "Plexar" resin marketed by Chemplex of Illinois of the United States of America. In a preferred method of manufacture of the multilayer film the layers, including the tie layers, are coextruded.

The heat-sealable polymer may be any of the conventional heat-sealable polymers well known in the packaging art preferably capable of forming seals of adequate strength at a temperature from about 90°C to about 120°C. Examples are low density polyethylene, an ethylene vinyl acetate copolymer, or an ionomer such as is marketed under the trade mark "Surlyn" by Du Pont of the United States of America. A particularly useful polymer for this purpose having a high degree of toughness and flexibility is a linear low density polyethylene alone or blended with other polymers such as low density polyethylene or ethylene/vinyl acetate. Such polymers are capable of forming seals of adequate strength under conditions of heat and pressure for usual packaging purposes, that is, seals of strength at ambient temperatures of at least 500 grams per 25 millimetres length of seal when measured by a seal peeling method.

The ethylene/vinyl alcohol copolymer layer preferably has a vinyl alcohol content in the range from 50 to 75% by weight to provide an oxygen barrier which is suitable for most packaging purposes where prevention of oxygen spoilage of the packaged contents is of prime importance.

The polypropylene layer preferably has an atactic content in the range from 15% to 20% by weight of the polypropylene. Such a layer is clear, tough and capable of being freely flexed without cracking. Further, since the melting point of the polypropylene layer is in the range from 150°C to 165°C, during the normal heat-sealing conditions of the multilayer film (that is, the temperature at which the heat-sealable polymer layer is sealed) the integrity of the multilayer film is maintained by the polypropylene layer while under tension and thus distortion of the layers in the heat-seal area is avoided.

The invention also includes a method of manufacture of a multilayer heat-sealable film having a high oxygen impermeability comprising bringing together into surface contact a surface layer of a heat-sealable polymer capable of forming seals of adequate strength with itself under pressure at a temperature within the range from about 80 to 130°C, an oxygen barrier layer of an ethylene/vinyl alcohol copolymer and a layer of polypropylene having an atactic content in the range from about 10 to 25% by weight.

The invention will now be more particularly described by way of the following Example.

Example

A multilayer film consisting of three layers adhesively bonded to each other by tie layers was formed by extrusion in a molten state of the materials specified below through a flat coextrusion die followed by quenching upon a chilled roller. The order of feed of materials to the die and the dimensions of the die was such that the multilayer film was 90 microns in thickness and was made up of five layers in the following order:

Layer 1 – 56 microns in thickness – a linear low density polyethylene having a heat-sealing temperature of 115°C.

Layer 2 – 4 microns in thickness – an adhesive (tie) layer of a low density polyethylene modified by grafting to provide polar groups marketed by Chemplex of Illinois, United States of America, under the trade name "Plexar 158".

Layer 3 – 6 microns in thickness – an ethylene/vinyl alcohol in which the vinyl alcohol content was 70%.

Layer 4 – 4 microns in thickness – an adhesive layer of "Plexar 158" as in Layer 2.

Layer 5 – 20 microns in thickness – polypropylene having an atactic content of 16% by weight as marketed by Badische Anilin Soda Fabrik of Ludwigshaven, Germany, under the trade mark "Novolen" and having a melting point in the range 157-162°C.

By "heat-sealing temperature" is meant the temperature at which two layers of the material under consideration will seal together to provide on cooling a sealed film combination which requires a force of 1000 gms per linear 25 millimetres of seal to peel the layers apart.

The resulting film was clear and was readily converted into pouches and/or bags on conventional pouch and bag making machinery at normal speeds without distortion in the seal area. The film exhibited a high degree of flexibility and durability in use substantially without any sign of cracking or pin-holing and had an oxygen permeability of 1.0 millilitres per square metre per 24 hours under a pressure difference of one atmosphere and with a relative humidity of 75%.

Although reference has been made to coextrusion through a flat die it will be understood that a similar five layered multilayer film may be prepared by extrusion through a tubular coextrusion die.

The multilayer films of the present invention are particularly suited for forming into bags for the packaging of liquids which are susceptible to spoilage by oxidation, for example, wine.

CLAIMS

1. A multilayer heat-sealable film having a high oxygen impermeability comprising a surface layer of a heat-sealable polymer capable of forming seals of adequate strength with itself under pressure at a temperature within the range from about 80 to 130°C, an oxygen barrier layer of an ethylene/vinyl alcohol copolymer and a layer of polypropylene having an atactic content in the range from about 10 to 25% by weight.

2. A film on which the heat-sealable polymer is capable of forming seals of adequate strength at a temperature within the range from about 90°C to about 120°C.

3. A film as claimed in claim 1 or claim 2 in which the adjacent layers are bonded together by a tie layer consisting of a polymeric adhesive.

4. A film as claimed in claim 1, claim 2 or claim 3 in which the heat-sealable layer is low density polyethylene, an ethylene/vinyl acetate copolymer, a linear low density polyethylene alone or blended with low density polyethylene or an ethylene/vinyl acetate copolymer, or an ionomer.

5. A film as claimed in any one of the preceding claims in which the ethylene/vinyl alcohol has a vinyl alcohol content from 50 to 75% by weight.

6. A film as claimed in any one of the preceding claims in which the polypropylene layer has an atactic content in the range from 15% to 20% by weight.

7. A method of manufacture of a multilayer heat-sealable film having a high oxygen impermeability comprising bringing together into surface contact a surface layer of a heat-sealable polymer capable of forming seals of adequate strength with itself under pressure at a temperature within the range from about 80 to 130°C, an oxygen barrier layer of an ethylene/vinyl alcohol copolymer and a layer of polypropylene having an atactic content in the range from about 10 to 25% by weight.

8. A method as claimed in claim 7 in which adjacent layers are bonded together by a tie layer consisting of a polymeric adhesive.

9. A method as claimed in claim 7 or claim 8 in which the film is formed by coextrusion of all the layers.

10. A method as substantially described in the specific Example.

11. A film when manufactured in accordance with the method as claimed in claim 7, 8 or 9.

12. A pouch or bag when manufactured from a film as claimed in any one of the claims 1 to 6 and 11.

Printed in the UK for HMSO, D8818935, 10 84, 7102.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

TO SEPARATE, HOLD TOP AND BOTTOM EDGES, SNAP—APART AND DISCARD CARBON

FORM PTO-892 (REV. 3-78) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

NOTICE OF REFERENCES CITED

SERIAL NO. 842,600 | GROUP ART UNIT 154 | ATTACHMENT TO PAPER NUMBER 5

APPLICANT(S) Shah

U.S. PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	NAME	CLASS	SUB-CLASS	FILING DATE IF APPROPRIATE
✓	A	4284674	8-1981	Sheptak	428	475.5	
✓	B	4355721	10-1982	Knott et al	428	35	
✓	C	4398635	8-1983	Hirt	206	532	
✓	D	4400428	8-1983	Rozenthal et al.	428	349	
✓	E	4407873	10-1983	Christensen et al.	428	35	
✓	F	4421823	12-1983	Theisen et al	428	349	
✓	G	4457960	7-1984	Newsome	428	35	
✓	H	4464443	8-1984	Farrell et al.	428	518	
✓	I	4495249	1-1985	Ohya et al.	428	576	
✓	J	4501797	2-1985	Super et al	428	349	
✓	K	4501798	2-1985	Koschak et al.	428	349	

FOREIGN PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	COUNTRY	NAME	CLASS	SUB-CLASS	PERTINENT SHTS. DWG	PP. SPEC.
	L								
	M								
	N								
	O								
	P								
	Q								

OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

R	
S	
T	
U	

EXAMINER T J Herbert Jr. | DATE 11/6/86 | ρ 10/2

*A copy of this reference is not being furnished with this office action. (See Manual of Patent Examining Procedure, section 707.05 (a).)

344

TO SEPARATE, HOLD TOP AND BOTTOM EDGES, SNAP—APART AND DISCARD CARBON

FORM PTO-892 (REV. 3-78)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

SERIAL NO. 842,600 | GROUP ART UNIT 154 | ATTACHMENT TO PAPER NUMBER 5

NOTICE OF REFERENCES CITED

APPLICANT(S) Shah

U.S. PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	NAME	CLASS	SUB-CLASS	FILING DATE IF APPROPRIATE
✓	A	4514465	4-1985	Schoenberg	428	516	5-20-84
	B	4532189	7-1985	Mueller	428	520	11-18-83
✓	C	4557780	12-1985	Newsome et al.	156	244.11	10-14-83
	D						
	E						
	F						
	G						
	H						
	I						
	J						
	K						

FOREIGN PATENT DOCUMENTS

*		DOCUMENT NO.	DATE	COUNTRY	NAME	CLASS	SUB-CLASS	PERTINENT SHTS. DWG	PERTINENT PP. SPEC.
	L								
	M								
	N								
	O								
	P								
	Q								

OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

R	
S	
T	
U	

EXAMINER T. Herbert Jr. | DATE 11/6/86 | p 2 of 2

*A copy of this reference is not being furnished with this office action. (See Manual of Patent Examining Procedure, section 707.05 (a).)

4/4

United States Patent [19]
Newsome et al.
[11] Patent Number: 4,557,780
[45] Date of Patent: Dec. 10, 1985

[54] METHOD OF MAKING AN ORIENTED POLYMERIC FILM

[75] Inventors: David L. Newsome, Neenah; Arnold R. Rein, Menasha; Bradley J. Hoss, Neenah; George O. Schroeder, Appleton, all of Wis.

[73] Assignee: American Can Company, Greenwich, Conn.

[21] Appl. No.: 542,031

[22] Filed: Oct. 14, 1983

[51] Int. Cl.[4] B29D 7/02
[52] U.S. Cl. 156/244.11; 156/244.24; 428/474.4; 428/475.5; 428/475.8; 428/516
[58] Field of Search 156/244.11, 244.14, 156/244.24; 428/474.4, 475.5, 475.8, 516

[56] References Cited

U.S. PATENT DOCUMENTS

2,773,285	12/1956	Piazze et al.	156/244.13
3,515,626	6/1970	Duffield	156/244.14
4,464,438	8/1984	Lu	428/516
4,469,742	9/1984	Oberle et al.	428/516
4,472,228	9/1984	Yoshimura et al.	156/244.24

FOREIGN PATENT DOCUMENTS

1949743	4/1971	Fed. Rep. of Germany	428/475.8
0121842	10/1978	Japan	156/244.11
0081156	6/1980	Japan	428/475.8

Primary Examiner—Caleb Weston
Attorney, Agent, or Firm—Stuart S. Bowie; Thomas D. Wilhelm

[57] ABSTRACT

Molecularly oriented plastic films have five molecularly oriented layers. A first layer provides a barrier to gaseous transmission through the film and has a composition of 0% to 50% nylon or nylon copolymer, and conversely 50% to 100% ethylene vinyl alcohol. Second and third adhesive layers are adhered to the surfaces of the first layer, and have compositions comprising olefinic polymers, or copolymers, or blends thereof, the compositions having carboxyl modifications therein. Fourth and fifth layers are adhered to the second and third layers on the respective surfaces opposite the first layer. The fourth and fifth layers comprise 40% to 100% ethylene vinyl acetate and 0% to 60% linear low density polyethylene. Also disclosed are processes for making the oriented five layer films.

23 Claims, No Drawings

METHOD OF MAKING AN ORIENTED POLYMERIC FILM

BACKGROUND OF THE INVENTION

It is highly conventional to utilize films of various oriented polymeric materials for the packaging of foods and like products. Although the necessary and desirable properties depend upon the specific applications for which the films are intended, normally they should exhibit good uniformity, strength, toughness, abrasion and flex-crack resistance, gloss, and heat stability. When formed into closed and sealed packages, such as by heat sealing, the packages should exhibit high burst strength and resistance to cutting, such as by metal closure clips. Also, because of the susceptibility of many food products to deterioration upon exposure to oxygen, it is often imperative that the film employed exhibit good barrier properties.

As is also well known, it is common practice to package meat and other food products in molecularly oriented films that can be shrunk upon exposure to heat. The need for good strength characteristics is particularly acute in such instances because of the vulnerability of the film to damage under the conditions of use.

Generally, the combination of characteristics necessary to provide films that are suited for use in many packaging applications is not afforded in a single layer product, and numerous multiple layer films have been developed or proposed.

Both the film producer and the film user require that oriented films satisfy a multiplicity of requirements. Of primary importance to the film user, in the case of shrink films, is the capability of the film to survive physically intact the processes associated with the film as a package, as it is filled, evacuated, sealed closed and heat shrunk. The film package must also be strong enough to survive the material handling involved in moving the contained product, which may weigh 100 pounds or more, along the distribution system to the next processor or to the user. Thus the package must physically protect the product.

It is often desirable to the film user that the package film serve as a barrier to infusion of gaseous materials from the surrounding environment. Of particular importance is provision of an effective barrier to infusion of oxygen, since oxygen is well known to cause spoilage of food products. The package should also be clear for product appeal purposes.

The film producer requires a film which can be produced competitively while meeting the performance requirements of the user. Thus the film materials should be readily extrudable, and susceptible to orientation, with sufficient leeway in process parameters as to allow for efficient film production. The process should also be susceptible to efficient extended production operations. In the orientation process, the film must be able to withstand the stretching. The orientation temperature should be a temperature which is economically achieved by the producer, and which provides for use of economical shrink processes by the film user.

Conventionally used shrink films are often produced and used as bags and have generally been constructed with ethylene vinyl acetate (EVA) and an oxygen barrier layer such as saran or ethylene vinyl alcohol (EVOH).

Notwithstanding the advantages, shrink film packaging, and particularly shrink bag packaging of meat, is not without its difficulties, many of which are attributable to limitations inherent in the films utilized for such applications. As will be appreciated, the processes of stretching the film, and later shrinking it, subject the film to rather severe conditions, due to the nature of the operations.

It is especially important to appreciate that the film is particularly vulnerable to failure at conditions of operation due to the relatively high temperatures to which it is subjected in the orientation and shrinking processes.

The film must be susceptible to orientation without distortion, or separation of the multiple layers which are normally present in films of this nature. The film must be strong enough, at the orientation temperature to withstand the the stretching without the creation of holes, tears, or nonuniform zones of stretching. In the case of blown tubular film, as in the well-known double bubble process, the film must be capable of physically supporting the stretching bubble during the orientation process. Finally, each of the layers of the film should be susceptible to orientation in the multiple layer film without fracture, separation, or creation of holes.

In shrink packaging use, the film must respond to heat rapidly enough for commercial practicality, and yet must not exhibit such a level of shrink energy as would cause the film to pull apart or delaminate during shrinkage, under its own internal forces. Moreover the shrink related problems may be seriously increased, for example, when a contained cut of meat includes protruding bones and/or significant depressions in its surface.

Prospective films are conveniently subjected to preliminary testing in a laboratory. In one such test, the prospective film is formed into packages by means of heat seals and air is injected into the packages. The recorded parameter is the air pressure that a given package successfully holds without failure of the sidewalls or the seals. Another convenient laboratory test measures the interlayer adhesions at the layer interfaces, by pulling apart the layers and measuring the force required for the pulling. The ultimate goal, of course, is to produce a sealed package, containing the contemplated product; and to have the sealed package, containing the product, retain its integrity as a sealed unit throughout the distribution and sale of the product, to the time of opening by the product user.

In the uses contemplated for oriented films of the invention, the most severe environments normally encountered by the films are those associated with the overall process of a packager, where films may be made into containers, containers are filled with product and are sealed closed, and may also be evacuated and/or heat shrunk. Thus the most significant test is to use the films in the commercial processing operations of a packager, to ascertain the overall reduction in the percentage of packages which leak.

Certain of the available 3-layer films having a saran layer are disclosed in Widiger et al U.S. Pat. No. 4,247,584. Those films provide a good balance of properties. Saran, however, has a number of its own problems. It has a brown color, which is generally undesirable. During extended extruder operation, bits of carbon form from decomposition of the saran in the extruder equipment, and later pass out through the die as undesired inclusions in the film. As a result, the operation must be shut down periodically for die cleaning. Finally, the power required to extrude saran is rela-

tively high. Thus, while saran is accepted as a functional material, alternate barrier material choices are desirable.

It is also suggested in the foregoing Widiger et al patent that a barrier layer of EVOH be used instead of the saran layer, so as to provide the excellent oxygen barrier properties of EVOH while avoiding the disadvantages of saran. And while EVOH does have certain problems associated with its fabrication and use, in certain applications it may be advantageously used.

In further improvement of the technology of oxygen barrier materials, oriented blends of EVOH are disclosed in copending application Ser. No. 290,171 by Schroeder et al, filed Aug. 5, 1981 and in copending application Ser. No. 290,172 by Newsome, also filed Aug. 5, 1981, both of common assignment herewith. The Schroeder et al application discloses oriented films of blends of EVOH and nylon along with plasticizers for the nylon. Newsome '172 discloses oriented films wherein EVOH is blended with any member of a family of polymers.

In another related application, Ser. No. 371,781 by Newsome, filed April 26, 1982, it is proposed that the inclusion of linear low density polyethylene (LLDPE) in at least one of the layers provides a significant decrease in the leaker rate when the film bags are used for shrink packaging of meat.

While the art of oriented multiple layer films is becoming crowded, there still exists a deficiency, as a need for easily produced oriented films which exhibit the afore-mentioned desirable properties. Particularly, there remain certain problems having to do with strength of the film and packages made therefrom and adhesion of the layers to each other at the layer interfaces, in addition to the typical problems with incompatibility of certain polymers with orientation. Thus it is desired to provide a film having improved strength properties imparted generally by creating a film having the desirable characteristics and imparting thereto properties of improved interfacial adhesion, and attendant improvements in the overall strength properties of such films as demonstrated in laboratory tests and in commercial use.

SUMMARY OF THE INVENTION

It has now been found that certain improvements are achieved in an oriented film comprising five polymeric layers wherein a first layer provides a barrier to gaseous transmission through the film and has a composition of 10% to 50% nylon or nylon copolymer, and conversely 50% to 90% of an ethylene, vinyl alcohol copolymer. The first layer has two opposing surfaces. Second and third adhesive layers are adhered to the surfaces of the first layer. The second and third layers both have compositions comprising olefinic polymers, or copolymers, or blends thereof, the compositions having carboxyl modifications therein. Fourth and fifth layers are adhered to the second and third layers on the respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% EVA and 0% to 60% LLDPE.

Each of the layers of the film is stretched in molecular orientation to substantially the same degree, and the layers are adhered to each other directly at the recited surface interfaces without the use of additional adhesive materials.

The oriented film is susceptible to being made into a closed and sealed container by means of heat seals formed about the periphery of adjacent superimposed sheets. The resulting container and its seals are capable of withstanding a high static internal gaseous pressure, up to at least as high as 29 pounds per square inch gauge (psi).

In some of the preferred structures the composition of the first layer is 30% to 50% nylon and 70% to 50% EVOH. An especially preferred composition for some structures is 40% nylon and 60% EVOH. A small residuum of EVA is also present as unused reaction component from the hydrolysis of EVA to EVOH.

The invention also includes a method of making five layer oriented films. In that method the film is first formed by being coextruded as a five layer structure and is subsequently oriented as a five layer structure. The coextrusion may be performed through a narrow straight slot die to form a flat sheet such as by cast coextrusion. Another means of forming the film is by coextruding it through a circular die to form a tube as by tubular extrusion, blown film extrusion, or water quenched tubular extrusion.

Where the film is formed as a flat sheet, orientation may be achieved as by compression rolling, by stretch orientation between a pair of nip rolls or by a tentering orientation process. Where the film is produced in tubular form, its orientation is preferrably effected by forming a bubble between two pairs of nip rolls and controlling the amount of orientation according to the amount of gas trapped in the bubble and by driving the nip rolls at different speeds as desired, to create longitudinal stretching of the film as well as the transverse stretching incurred primarily by means of the gas entrapped in the bubble. The entire method of producing the film includes coextruding a five layer film, cooling the coextruded film, reheating the film to orientation temperature, molecularly orienting the film, and cooling the oriented five layer film.

Particularly where the film is to be produced using tubular processes and where the tube is to be inflated or oriented in tubular form, it is desirable that the fourth and fifth layers include at least 10%, and preferrably 25% to 40% LLDPE as a blend material with EVA.

The selection of the specific compositions of the adhesive materials for the second and third layers depends to some extent on the compositions of the first, fourth and fifth layers, and on the processing conditions, including the coextrusion and orientation processes. It is necessary that the second and third layer compositions include carboxyl modifications. Exemplary of these modifications are organic acids and anhydrides. Preferred materials are olefinic, of which specific examples are low density polyethylene (LDPE), medium density polyethylene (MDPE), EVA, and LLDPE, all having the recited carboxyl modifications. Blends of modified olefins may also be advantageously used.

The invention is further embodied in a closed and sealed bag. The fabrication of the bag from the film is most easily accomplished when the film is extruded and oriented as a continuous tube. The bag is formed by severing a length of the tubular film, across its transverse dimension, from the continuous tube. The severed portion is essentially a collapsed cylinder with both ends open. The fabrication of a bag is completed by forming a heat seal across one end of the collapsed cylinder. The other end is left open for loading of product. When the product has been loaded, the bag is then evacuated, a clip is put in place on the unsealed end, and the bag is heat shrunk. Alternately the final closing seal

may be made by, for example, a separate heat sealing process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Each of the five polymeric layers in the films of this invention must satisfy certain specific functional requirements as described hereinafter. The first layer is generally known as the core layer and has two layers on each of its surfaces, such that, in traversing through the thickness of the film from either outside surface of the film, two other layers are traversed before the first layer is encountered. The composition of the first layer is selected to provide functional packaging properties, in the film, that impede oxygen transmission, and to lend toughness to the layer, particularly in the plastic state, to facilitate handling of the film during film production. It will be appreciated that desirably the composition of each layer imparts some degree of toughness to the film for ease of film production. The thicknesses of the first, fourth and fifth layers, however, cause them to be the layers most susceptible to improvements in toughness by proper selection of polymer composition, so usually these are the layers for which such improvements are sought.

THE FIRST LAYER

Returning to the discussion of the first layer, there is included therein at least 50%, and preferrably at least 60% of an EVOH. The fractional amount of EVOH in the first layer determines to a significant degree the overall effectiveness of the film in impeding transmission of oxygen. While as little as 20% EVOH in the first layer composition does improve the oxygen transmission rate over a nylon composition without EVOH, it is usually desirable to have at least 50% EVOH in the composition to impart the desired superior oxygen barrier property generally associated with EVOH. Therefore, 50% EVOH represents a preferred lower limit to the amount of EVOH. Higher levels of EVOH are advantageously utilized. While up to 90% EVOH is acceptable for the purposes of the invention, little added benefit of oxygen transmission barrier is achieved at levels of over 70% EVOH, and 60% EVOH is generally believed to provide the most efficient usage. The EVOH typically has a molecular weight in the range of about 20,000 to 30,000 and a melting point temperature of about 325° to 375° Fahrenheit, these characteristics corresponding roughly to melt indices of about 9 to 1.5. The melt index values herein are determined in accordance with ASTM Test D-1238, Procedure E or L, using a weight of 2160 grams and temperature of either 190° or 210° Centigrade, as appropriate. Typically, the EVOH has a density of 1.1 to 1.2. Suitable temperature for processing the EVOH is about 400° to 480°, and preferrably 410° to 440° Fahrenheit. While the degradation temperature of EVOH is generally regarded to be about 450°, this is not inconsistent with the higher processing temperatures herein, due to the short residence time in the extrusion process. Illustrative of EVOH resins that are suitable for use are those available from Kuraray and from Nippon Gohsei, both of Japan. The products of the former company are EP-E and EP-F, and those of the latter company are designated SOARNOL-D, SOARNOL-E, and SOARNOL-ET. EP-E and EP-F contain about 55% and 68% vinyl alcohol, respectively, in the molecule and have melt flow values, as determined at 190° Centigrade, of 5.8 and 1.5 respectively. SOARNOL-D, SOARNOL-E, and SOARNOL-ET contain 71%, 62% and 62% vinyl alcohol, respectively, and exhibit melt flow values of 7.4, 8.0 and 3.5, respectively, as determined at 210° Centigrade.

After accounting for the presence of the EVOH, the balance of the composition of the first layer is a plasticized nylon. The inclusion of nylon generally imparts the property of toughness, while reducing the amount of the more expensive EVOH which is used. Structural properties of improved toughness of the first layer composition as compared to 100% EVOH are discernible with as little as 10 weight percent nylon, based on the total layer composition. However, it should be appreciated that the incorporation of nylon in virtually any concentration is generally of some benefit, in improving orientation processing as well as enabling cost reductions to be realized.

A surprising feature of the films of the invention resides in the fact that as much as 30 weight percent nylon can be included in the blend composition of the first layer without reducing the effective oxygen barrier properties of the EVOH resin significantly. This has been found to hold generally true regardless of the nature of the nylon used, or of any additives which may be incorporated into the nylon.

While the polycondensation resins such as nylon 66 may be employed to advantage, for most purposes the addition polymer nylon 6 is preferred. To be suitable for such use, the nylon generally has a molecular weight in the range of 20,000 to 30,000 and a melting point temperature of about 415° to 440° Fahrenheit, with a melting point temperature of about 428° being optimal in many cases. Such nylon resins are normally processed at temperatures of about 510° to 540°, thus presenting a fundamental difficulty which is addressed in U.S. Pat. No. 4,347,332, issued Aug. 31, 1982, to Odorzynski and Knott. As taught therein, the provision of a nylon-/EVOH blend which can be extruded at temperatures below the degradation temperature of EVOH is achieved by the incorporation into the composition of an agent that serves as an effective plasticizer for the film-forming nylon. While some of the agents utilized may not previously have been regarded as plasticizers, in the the present blends of the first layer herein, they do appear to perform that function. It appears that the plasticizing agents are capable of intermolecular hydrogen bonding and disruption of crystallinity within the blend structure, to effectively lower the temperature at which processing can be carried out. As a result, film-forming nylons that normally process at temperatures of about 510° to 540° Fahrenheit become processable in these blend compositions at temperatures that are considerably lower and that are, in fact, within a range of temperatures at which the EVOH is also processable and not subject to significant degradation. More particularly, the externally plasticized film-forming blend compositions of nylon resins and EVOH resins, so plasticized, are processable at temperatures of about 400° to 480° Fahrenheit, with preferred temperatures being about 410° to 440°.

The amount of plasticizer used may vary between fairly wide limits, and as little as 2 percent or as much as 25 percent, based upon the weight of the nylon resin, may be acceptable. For satisfactory results, it is usually necessary to use a concentration of plasticizer in excess of 2 percent, and 5 weight percent usually represents a preferred lower limit for such blends. Amounts of plasticizer in excess of 15 weight percent normally produce

little added benefit, insofar as processing is concerned and therefore that concentration represents a preferred upper limit. The amount of plasticizer utilized in any given case, of course, depends upon a number of factors, including the composition of the nylon film-forming resin and of the specific plasticizer employed, the actual processing temperatures involved, and the like.

Specific plasticizers preferred fall into three main categories, namely the long chain fatty acid amides, (i.e. those containing 16 to 18 carbon atoms in the chain), the aromatic sulfonamides, and the nylons and nylon copolymers which exhibit a melting point temperature of less than about 400° Fahrenheit. Within these categories, the most desirable plasticizers are lauramide, o,p-toluenesulfonamide, N-ethyl-o, p-toluenesulfonamide (the two sulfonamides of course being mixtures of the ortho and para isomers), and nylons such as nylon 6/36, nylon 11 and nylon 12 having molecular weights of about 7,000 to 10,000. Other suitable products that can be used as plasticizing agents include nylon 11 and nylon 12 of about 25,000 molecular weight and melting at temperatures of about 370° and 350° Fahrenheit, respectively, 2,2,4-trimethyl-1, 3-pentane-diol, cumyl-phenyl-benzoate, and a product offered commercially by Paul and Stein Brothers of New York, New York under the designation STYSOLAK AW, referred to as a polyethylene oxide.

The blends utilized to produce the first layer of the oriented films of this invention may utilize what may be regarded as internally plasticized nylon rather than incorporating such a component as an independent third ingredient (i. e. in addition to a film-forming nylon and the EVOH copolymer). The internally plasticized nylons may be either random or block copolymers, or they may be alloys of a nylon resin with an alloying resin. In any event, it is believed that the comonomer or the alloying resin, as applicable disrupts the crystalline structure of the relatively high melting nylon constituent and/or undergoes hydrogen or other secondary bonding so as to produce the desired effect. As will be appreciated, the ultimate objective is to provide a nylon ingredient which is processable at approximately the temperature at which the EVOH can be processed. Nylon copolymers that are suitable for use without added plasticizers include nylon 6/12; 6/36; and 6/66; the primary factor being that the copolymer has a melting point temperature below about 400° Fahrenheit. For some applications a low melting nylon (e. g. nylon 11 or nylon 12) can be used, without modification or added plasticizer, in combination with the EVOH. It may alternately be blended in virtually any proportion with a higher melting nylon, such as nylon 6, to form the nylon component of the nylon/EVOH blend.

In producing the externally plasticized blends of the invention it will generally be desirable to premix the plasticizer with the film-forming nylon, so as to ensure maximum effectiveness in producing the desired result. This may be done in a compounding extruder or the like, depending to some extent on the physical state of the additive. It is generally most advantageous to produce pellets of such plasticized nylon, which can then be admixed with pellets of the EVOH prior to introduction into the extruder that is to be used for production of the first layer.

THE SECOND AND THIRD LAYERS

The second and third layers of the film serve generally the function of providing adhesion between the first

layer and the fourth and fifth layers. Dispositionally, the second and third layers are located between the first and fourth layers and the first and fifth layers, respectively. As is clear from the above description of the first layer, and as will be clear from the following description of the fourth and fifth layers, the compositions of the first, fourth, and fifth layers can vary somewhat independently of each other, within relatively broad ranges. Thus the examples which follow herein are considered illustrative, only, of the adhesive compositions and processes which are useful in making films of this invention. In general, the adhesives of this invention are basically olefinic polymers or copolymers having carboxylic modifications thereto. The preferred basic polymers are LDPE, LLDPE, MDPE and EVA. The preferred carboxylic modification is an organic acid or anhydride, and particularly maleic anhydride.

Specific adhesive polymers which have an LDPE as base polymer and which exemplify the desired compositions of the second and third layers, are Novatec AP220L available from Mitsubishi Chemical Industries Company, and PX-158-5, available from Chemplex Company. An LLDPE-based adhesive polymer is available from Mitsui Company, Japan, as Admer NF-500. Resins based on MDPE are Novatec AP212H and AP460H, for example. Resins based on EVA are Admer VF-500 from Mitsui Company, PX-3 and PX-100 from Chemplex Company, and CXA 3101 from DuPont Company. Another olefinic based resin containing vinyl acetate moieties is CXA E-136 from DuPont. In some cases it will be found advantageous to provide as an adhesive layer a blend of polymers. It may be a blend of more than one of the adhesive polymers; it may be a blend of, for example, the selected adhesive polymer with material such as is incorporated into the adjacent layers. Indeed, it may be a blend of a combination of adhesive polymers and material substantially the same as that in the fourth or fifth layers. Thus it is conceivable that the second or third layer, or both, could comprise fractional amounts of polymeric material either identical to or very similar to those materials used in the compositions of the adjacent layers—i. e. the first, fourth, and fifth layers, as applicable.

THE FOURTH AND FIFTH LAYERS

The fourth and fifth layers serve generally as the outer layers of the film. The compositions of the fourth and fifth layers are 40% to 100% EVA and 60% to 0% LLDPE. The fourth layer is generally designed to have heat sealable properties for the purpose of making a sealed container by means of heat seals. The fifth layer is disposed on the opposite surface of the film from the fourth layer, and in a formed container, serves as the outer layer of the container. In the formed container, the fifth layer serves a primary function of protecting the package and its product from physical abuse.

The compositions of the fourth and fifth layers may or may not be the same so long as each composition is within the compositional parameters given herein. The EVA provides high levels of adhesion at the interfaces of the fourth and fifth layers with the second and third layers. EVA's, particularly those having greater than 85% ethylene, also provide substantial structural strength to the film during the orientation process, and are especially beneficial for the orientation of tubular films. The ability of EVA to provide processing strength for the film manufacture is most efficiently used where high levels of EVA are present in the fifth

layer. The LLDPE is highly desired for its capability of surviving intact the processes involved in shrinking those films which are formed into sealed containers and shrunk by a heat shrinking process. In general, the ability of, for example, a shrink bag to withstand the shrinking process correlates directly with increasing percent LLDPE, up to about 50% to 60% LLDPE. Films having 25% to 40% LLDPE in at least one of the fourth and fifth layers show marked shrink strength improvement over films without LLDPE. Films having higher percentages of LLDPE, such as 40% to 60% in at least one of the fourth and fifth layers, have even better shrink performance, but are increasingly more difficult to stabilize in the manufacturing process, the degree of difficulty increasing with increased percentages of LLDPE. Because of manufacturing processes, layer compositions having greater than 60% LLDPE are not preferred.

The overall thickness of films of this invention is nominally the same as the thickness of conventional oriented films used for shrink packaging. Films are generally about 2.25 mils thick, with a normal range of 1.5 to 3.0 mils. Films thinner than 1.5 mil tend to be too weak to perform all required functions. Films thicker than 3.0 mils are economically unable to compete with thinner, competitive films, though film thicknesses up to 8–10 mils will be functionally acceptable, and may be preferred where other speciallized packaging properties are required.

As regards preferred thicknesses of the individual layers for a 2.25 mil film, the first layer is 0.15 to 0.30 mil thick. The second and third layers are both about 0.10 mil, just thick enough to provide a continuous layer. The fourth layer is the thickest layer of the film and is 1.25 to 1.40 mil. The fifth layer is about 0.50 mil.

LLDPE polymers suitable for use in the fourth and fifth layers are those having a melt index (MI) of up to about 6. Preferred LLDPE polymers have an MI of 0.5 to 1.5. Among the preferred polymers are DOW 2045, DOW XD-61508.01 and DuPont 11P. A modified LLDPE polymer, Admer NF-500, is also technically suitable, though its price usually prevents its use in the fourth and fifth layers.

EVA's preferred for use in the fourth and fifth layers are those having 6% to 12% vinyl acetate (VA) content and a melt index less than 1. While blend amounts are shown herein in weight percent, VA contents are mole percent. Especially preferred EVA's have VA content of 7% to 9% and melt index of 0.2 to 0.8.

While acceptable 3-layer subcombinations of the 5-layer films of the invention are difficult to make, as described hereinafter, the 5-layer films described herein surprisingly have been discovered to be susceptible to being manufactured according to conventional orientation processes. Thus there appears to be a special cooperation among the layers of the 5-layer films that is not present in 3-layer films and 3-layer subcombinations of the 5-layer films. In the following examples a few films are described in detail as being manufactured using equipment common to the "double bubble" process. Films of the invention may be made by this process, or other conventional processes. The process of making films or bags of this invention need not include exposing the film to ionizing radiation, for example in dosage amount of 3 megarads or more. Choice of the desired process depends not only on the film composition and structure but also on specific properties desired. In light of the disclosure herein, the choices on any particular film are now a matter of engineering selection.

Molecular orientation of the films of the invention may be effected utilizing any suitable technique, which depends somewhat on the structure of the film and the nature of the components of which it is comprised. It is believed that, in general, the most practical manner of extruding and orienting the film is by the so-called "double bubble" technique. As is well known, in such a method the film may be extruded downwardly as a tube formed by an annular die, and carried into a water quench tank, generally with a cascade of water on the outside surface of the tube to provide initial cooling. The tube is flattened in the quench tank, is withdrawn from the quench tank, and is reheated (normally in a second water bath) to its orientation temperature. It is then stretched in the machine direction between two sets of rolls that are so rotated as to establish a linear rate differential therebetween, and is simultaneously oriented in the cross-machine direction as an inflated bubble trapped between the nips of the rolls. In accordance with conventional practice, the film is usually cooled by air in the orientation zone.

In the orientation process, the film is typically stretched in both the machine direction and the cross machine direction. Convenient orientation ratios in both directions are 2/1 to 4/1. Preferred orientation temperatures are 206°–212° F. While the temperature is adjusted in accordance with the film composition, a most preferred orientation temperature for many of the films of the invention is 210° F.

EXAMPLE 1

A mixture for use as the composition of the fourth and fifth layers is made by dry blending a pellet mixture of 75% NORCHEM NPE-493 EVA and 25% DOWXD-61508.01 LLDPE. The composition of the first layer is a blend of 60% SOARNOL-E EVOH and 40% Custom 615I, nylon 6, made by dry blending the pellets of the respective polymers. The second and third layers are Novatec AP220L. A first extruder is charged with the EVOH-nylon blend to form the first layer. Second and third extruders are charged with AP220L to form the second and third layers. Fourth and fifth extruders are charged with the blended pellets of EVA and LLDPE to form the fourth and fifth layers. Using the five extruders, a five layer tube is downwardly coextruded. A water cascade cools the film initially as it exits the die. Cooling of the tube is completed in a water quench tank. The tube is then reheated to a temperature of 210° F., and is oriented as an inflated bubble at ratios of approximately 2.5/1 in the machine direction and 3.5/1 in the cross machine direction. The oriented film is cooled, the bubble collapsed, and the film wound up. In the resulting film the thicknesses are:

first layer—0.30 mil
second layer—0.10 mil
third layer—0.10 mil
fourth layer—1.25 mil
fifth layer—0.50 mil

EXAMPLE 2

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are Admer NF-500, LLDPE.

EXAMPLE 3

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are Admer VF-500, EVA.

EXAMPLE 4

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are Chemplex PX-3 EVA.

EXAMPLE 5

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are Chemplex PX-158-5 LDPE.

EXAMPLE 6

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are Chemplex PX-100 EVA.

EXAMPLE 7

An oriented five layer film is made as in EXAMPLE 1 except that the second and third layers are DuPont CXA E-136 modified polyolefin.

EXAMPLE 8

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are DuPont CXA 3101 EVA.

EXAMPLE 9

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the first, fourth, and fifth layers are changed. The first layer is 60% SOARNOL-ET EVOH and 40% UBE 5033B nylon 6/66 copolymer. The fourth and fifth layers are 75% USI UE-80232 EVA and 25% DOW XD-61508.01 LLDPE.

EXAMPLE 10

An oriented five layer film is made as in EXAMPLE 9 except that the compositions of the second and third layers are DuPont CXA E-136.

EXAMPLE 11

An oriented five layer film is made as in EXAMPLE 9 except that the compositions of the second and third layers are Novatec AP212H, MDPE.

EXAMPLE 12

An oriented five layer film is made as in EXAMPLE 9 except that the compositions of the second and third layers are Novatec AP460H, MDPE.

EXAMPLE 13

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are Novatec AP212H, MDPE.

EXAMPLE 14

An oriented five layer film is made as in EXAMPLE 1 except that the compositions of the second and third layers are Novatec AP460H, MDPE.

EXAMPLE 15

An oriented five layer film is made as in EXAMPLE 10 except that the thickness of the fifth layer is increased to 8.25 mils so that the finished thickness of the film is 10 mils.

Table 1 shows data for each of the polymers used in the above examples.

TABLE 1

Polymer	Base Resin	VA Content	Melt Index
USI NA 235	EVA	4.5%	0.35
USI UE 657	EVA	12.0%	0.50
USI UE 80232	EVA	9.0%	0.40
NORCHEM NPE 493	EVA	8.0%	0.50
DOW XD-61508-01	LLDPE	NA	1.20
CUSTOM 615 I	NYLON 6	NA	3.19*
UBE 5033B	Nylon Copolymer	NA	—
NIPPON GOHSEI SOARNOL-E	EVOH	NA	5.50
NIPPON GOHSEI SOARNOL-ET	EVOH	NA	2.70
	Adhesive Polymers		
ADMER VF 500	vinyl acetate copolymer	—	2.20
DU PONT CXA 3101	vinyl acetate copolymer	—	3.50
DU PONT CXA E-136	Modified Polyolefin	yes	2.50
CHEMPLEX PX-3	EVA	9.0	3.00
CHEMPLEX PX-100	EVA	12.0	0.85
CHEMPLEX PX-158-5	LDPE	NA	1.80
NOVATEC AP220L	LDPE	NA	1.76
NOVATEC AP212H	MDPE	NA	0.70
NOVATEC AP460H	MDPE	NA	5.60
ADMER NF 500	LLDPE	NA	2.00

*Solution viscosity.

Films made according to EXAMPLES 1–10 were tested for layer adhesion on an Instron Tensile Tester at a crossing head speed of 10 inches per minute. Test strips of film were cut six inches long by one inch wide with the length of the strips running in the machine direction of the film manufacturing process. Separation of the layers at their respective interfaces was initiated by one of two methods. In the first method, a piece of tape was adhered on each side of the film near the film edge and then the tapes were pulled apart. In the second method, the end of the sample strip was dipped into a solvent bath of 1, 1, 1, trichloroethane until the layers began to separate. The critical interlayer adhesions, those being the ones between the first and second layers, and between the second and fourth layers, are shown in Table 2 below. "Core" refers to the first layer. "Tie" refers to the second layer. "Inner" refers to the fourth layer.

TABLE 2

		Layer Adhesion	
Example	Tie Layer	Core/Tie (inner)	Tie/Inner
1	AP 220L	553	CNS
2	NF-500	785	CNS
3	VF-500	CNS	46
4	PX-3	760	CNS
5	PX-158-5	CNS	360
6	PX-100	115	CNS
7	CXA E-136	CNS	CNS
8	CXA 3101	88	CNS
9	AP 220L	CNS	CNS
10	CXA E-136	384	354

CNS = cannot separate. All specimens tore on Instron.

In a study of interlayer adhesions, three layer films were made wherein one of the surface layers was comprised of an adhesive polymer as in TABLE 1. The adhesive polymer layers were 0.6 mil thick. The core layers were 0.3 mil thick and were comprised of 60%

SOARNOL-E and 40% Emser F47 nylon 6. The other surface layer of the film was 1.35 mil thick and comprised 70% EVA and 30% LLDPE.

In the first film, the adhesive polymer used for the second and third layers was CXA 3101. The film was hazy and tacky, and the resulting film had a wrinkly, non-uniform appearance. Though this film was considered unacceptable because of its appearance, it was tested for interlayer adhesion at the adhesive polymer layer interface. That adhesion was 74 grams.

In the second film, the adhesive polymer was Plexar 100. This film was processed satisfactorily and had an acceptable appearance, and a favorable layer adhesion of 116 grams.

In a third film, the adhesive polymer was Plexar 3. This film was processed satisfactorily and had a good appearance, but the interlayer adhesion was only 34 grams, dramatically lower than the 760 grams attained in the comparable 5-layer film of EXAMPLE 4.

Regarding burst strengths of bags made from the films of the invention, it was expected that strengths would be related to the interlayer adhesions as shown in Table 2. For instance, the films of EXAMPLES 3 and 8 each have weak adhesion at one interface. It would be expected that these films would be too weak to function normally such as for forming sealed containers. From past experience with 3-layer films, it is known that at least 100 grams, and preferrably 300 grams, of adhesion is desired.

Sealed bag containers were fabricated from films of EXAMPLES 1–10 by making heat seals about the periphery of respective overlapping terminal edges. It was unexpectedly found that all the films of the examples formed good heat seals in forming sealed film packages by well-known heat sealing techniques. The films of all the examples herein could not be broken at pressures of 29 psi. Packages made from film of EXAMPLE 12 were inflated to 45–55 psi before the seals failed.

As a comparison, a three layer oriented film having the structure EVA/EVOH/EVA was prepared and tested. The EVOH layer was 0.2 mil. The EVA layers were 0.6 and 1.45 mils thick, for an overall film thickness of 2.25 mils, the same thickness as in EXAMPLES 2–11. Thirty bags were tested in each of two bag sizes, 14"×28" and 22"×36". The range of burst strengths were 19–25 psi for the 14 inch bags and 18–24 lbs. for the 22 inch bags. Average burst strengths were 22.65 psi and 20.73 psi for the 14" and 22" bags respectively.

Regarding clip cut performance, bags made from the films of EXAMPLE 9 were tested on four clipping machines in a trial in a commercial plant. Clipping pressures and spikes were:

Machine No.	Clip Pressure	Spike
1	1350	60
2	1400	25
3	1425	50
4	1475	25

Out of 381 packages processed, only 4 packages were unacceptable because of clip cuts, for a highly satisfactory reject rate of 1%. Laboratory clipping trials on three-layer films of the structure /EVA/EVOH-/EVA/, wherein EVOH included several EVOH blends, showed a wide range of clip cut failures at 1700 psi clip pressure, 100 psi spike; on a 14-inch bag. Average clip cut failure for 24 varieties of 3-layer structure was 66%. On 22-inch bags, the average failure rate is expected to approach 100%.

One of the films in the above iterated clipping trials on 3-layer films had a core layer composition of 50% EVOH and 50% nylon. Its clip cut failure rate was 33%, whereas the failure rate for the five layer structure was 1%. Thus the addition of the second and third adhesive layers, while it did not always provide strong interlayer adhesion after the orientation process, it did provide uniformly strong heat seals, and excellent clip cut resistance.

In another plant trial, bags made from the films of EXAMPLE 9 were loaded with beef, sealed closed and heat shrunk. The bags had excellent seal properties. (The particular line on which the bags were tested had been experiencing a normal leaker rate of 8% to 15% using conventional bags having a three layer structure of /EVA/Saran/EVA/.) After being filled with meat, the bags were evacuated, heat sealed by a heat sealing bar, and heat shrunk at 200° F., all according to the normal operational practice on that line. In a test run of 1000 experimental bags made according to EXAMPLE 10, the leaker rate was only 4.5%.

The description herein has emphasized heat shrinkable films, and particularly those associated with meat packaging. The films of the invention may also be fabricated with use of a thermal operation known generally as "heat setting," wherein, after the film is oriented, it is held under moderate tension at an elevated temperature of about 210° Farenheit for about 2 to 10 seconds whereby the elastic memory of the film is relieved and the film loses its heat shrinking capability. Such films are dimensionally relatively stable at elevated temperatures. Such films may be preferred in packaging end use where heat shrinkage of the film is generally not preferred.

In making a bag, it is entirely satisfactory to start with a sheet of film and fold it over onto itself, with the fourth layer to the inside, and form heat seals along the terminal edges of the two opposite open sides to effect fabrication of a bag. After product has been inserted, the closing and sealing operation is the same as for a bag formed from tubular film.

While the films herein have been described as being preferrential for use as a bag, they may be used as sheet film as well.

Also it is completely acceptable, and within the realm of the invention, to utilize the films described herein as a subassembly of a more complex film. Other layers may be adhesively mounted thereto. Particularly with regard to the heat set films, other layers may be added by thermal processes such as extrusion laminating, extrusion coating or combining at a nip with a combination of heat and pressure.

Other variations of the invention, in both the articles and the methods will now be obvious to those skilled in the art.

Having thus described the invention, what is claimed is:

1. A method of making a five layer oriented polymeric film, said method comprising the steps of:

(a) coextruding a five layer film having a first barrier layer, the composition of said first layer being 10% to 50% nylon or nylon copolymer and 90% to 50% ethylene vinyl alcohol, said first layer having two opposing surfaces; second and third adhesive layers adhered to said surfaces of said first layer, said second and third adhesive layers both comprising olefinic